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HIGH-SPEED ELECTRON-BEAM LITHOGRAPHIC RESISTS FOR MICRON AND SU--ETC(U)  
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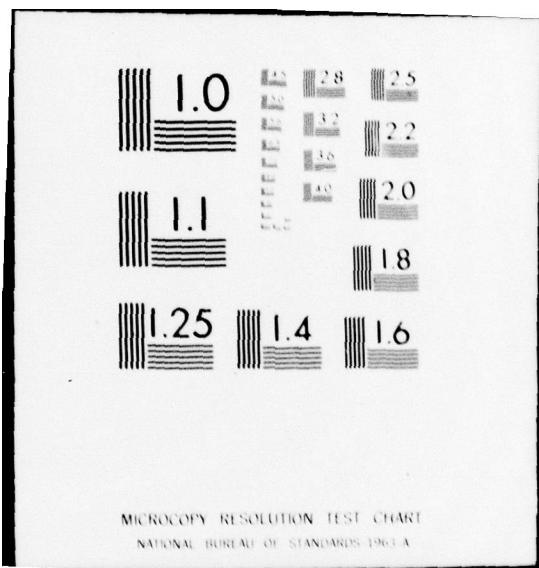
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(6) HIGH-SPEED ELECTRON-BEAM LITHOGRAPHIC RESISTS FOR  
MICRON AND SUBMICRON INTEGRATED CIRCUITS (u)

(11) JUN 1978

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(12) 11 P.M.

#### INTRODUCTION

Next-generation RADAR and ELINT systems are planned to provide the field commander with comprehensive intelligence on the disposition of enemy weapons and electronics equipment. Ultra-compact signal processors with unprecedented capabilities are the heart of these systems. Fabrication of the required high-density integrated circuits (IC's), with elements in the micron to submicron range, is beyond the resolution limit of state-of-the-art optical photolithography. Electrons with 10-20 keV energies can be accurately focused to beam diameters much less than a micron. Electron-beam lithography (EBL) meets the projected resolution requirements, and is expected to be a key technology for the production of sophisticated new digital communications systems for the Army.

Like the photolithographic IC production technique, EBL is also totally dependent upon organic polymer resists for pattern delineation. In EBL processing, a 5,000-10,000 Å resist film is spun onto the monolithic IC substrate. IC patterns are then written into the resist with the finely focused electron beam. E-beam irradiation decreases or increases the resist molecular weight, which, in turn, increases or decreases the dissolution rate relative to the unirradiated portion of the resist layer. When the irradiated resist pattern dissolves at a faster rate, an indented image is formed, and the resist is termed a positive acting resist (see Figure 1). If the opposite occurs, the resist is termed to be negative in function (see Figure 2).

Economical EBL production hinges upon the resist sensitivity,

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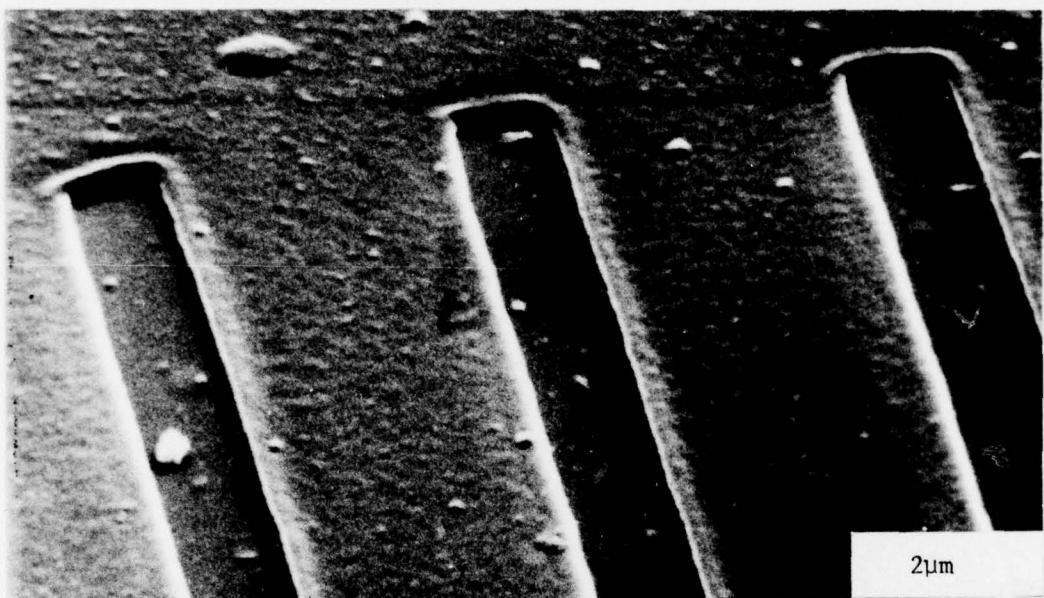


Figure 1. Scanning electron micrograph of developed electron-beam etched lines in poly(methyl methacrylate).

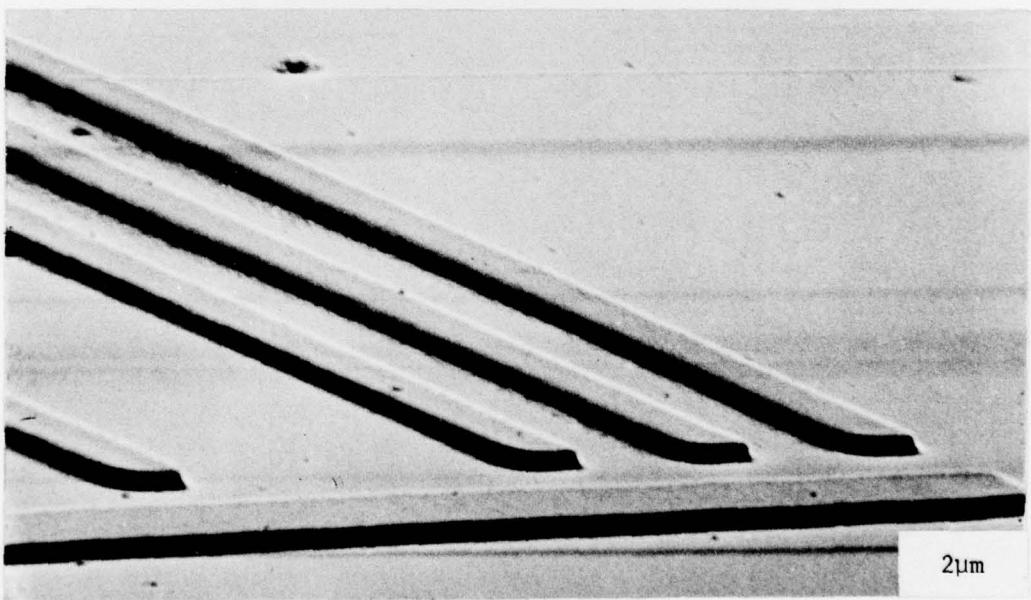


Figure 2. Scanning electron micrograph of developed electron-beam etched lines in poly(alpha-chloroacrylonitrile).

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which governs the electron writing time per wafer. The objective of our work is a set of sensitive resists with varying properties for the production of next-generation high-performance military IC devices. Early efforts in this technological area have been largely based upon the availability of commercial polymers. In this work, we apply basic radiation-chemistry principles, which were more or less disregarded previously, to devise and develop high-merit polymer resists.

#### RADIATION EFFECTS AND MEASUREMENT TECHNIQUES

When a polymer resist is irradiated in-vacuo with 10-20 keV electrons (or equivalent gamma-irradiation), both chemical and physical changes occur. First, the polymer molecular weight changes due to bond-scission or crosslinking.

Changes in number-averaged molecular weight,  $\bar{M}_n$ , obey the equation: (1)

$$\bar{M}_n^{-1} = \bar{M}_{n,0}^{-1} + [G_s - G_x] D / 100 N_A \quad (1)$$

where  $G_s$  and  $G_x$  are the radiation scission and crosslinking yields per 100 eV absorbed dose,  $N_A$  Avogadro's number, and  $D$  the radiation dose. Similarly, the weight-averaged molecular weight,  $\bar{M}_w$ , follows the equation: (2)

$$\bar{M}_w^{-1} = \bar{M}_{w,0}^{-1} + [G_s - 4G_x] D / 200 N_A \quad (2)$$

Thus if  $(\bar{M}_n^{-1})$  and  $(\bar{M}_w^{-1})$  are followed as a function of dose,  $G_s$  and  $G_x$  may be obtained from the slopes of the two independent determinations. Values of  $\bar{M}_n$  are usually obtained by membrane osmometry, while  $\bar{M}_w$  is obtained by either gel permeation chromatography (3) or light scattering techniques (3). For  $G_s$  predominant the resist is positive; for  $G_x$ , negative.

When polymers undergo radiation-induced main-chain scissions, the formation of free radicals is a consequence. Under certain conditions some of these radicals are stable enough to be observed by electron paramagnetic resonance techniques (4). As in scission and crosslinking radiation processes, radiation-scission radical values,  $G$ (rads), can be measured. Polymers with high  $G$ (rads) are also found to have high  $G_s - G_x$  or  $G_s$  (5).

The last technique, but most important to electron resist researchers, is the direct e-beam sensitivity ( $Q$ ) method.  $Q$  is the total absorbed e-beam dose in coulombs/cm<sup>2</sup> and is measured by scanning

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electron microscopy techniques. For a positive resist,  $Q$  is defined as the dose at which 20% of the unexposed resist is removed during development for complete dissolution of the irradiated beam pattern area. This is also equivalent to a dissolution rate ratio,  $d_{irradiated}/d_{unirradiated}$  (6), of 5. For a negative resist,  $Q$  is defined as the dose at which a 50% thickness of irradiated resist remains following total development dissolution of the unexposed resist portion.

All of the techniques discussed above are capable of measuring the radiation degradation or crosslinking susceptibility of a polymer resist system. The independent  $G$  values have been found to be well correlated (7).

#### POLYMER RESIST STRATEGY

Before directly testing a polymer as a predetermined type of a resist, an arduous and time-consuming task, the radiation behavior of that polymer should be reviewed if it has been previously investigated. If it hasn't been studied at the basic level, it is probably time-efficient to do one or more of the measurements described in Radiation Effects and Measurement Techniques, than to proceed to direct testing. This is, in fact, how resist research at ET&DL is carried out. The basis for several of the e-beam resists utilized today can be found in the basic polymer radiation chemistry papers published between 1958 and 1973.

Wall (8) and Miller et al (9) observed very early that vinyl polymers of the form  $-(CH_2-C(X)Y)_n$ , where X nor Y is hydrogen, degrade preferentially when subjected to ionizing radiation in vacuo. Polymethyl methacrylate (PMMA)  $-(CH_2-C(CH_3)CO_2CH_3)_n$ , a high-resolution positive e-beam resist, is an example; PMMA has a  $G_S$  value of 1.3 (10), a  $G_X$  value of zero (11), a  $G(CO_2CH_3)$  of 1.0 (12), and  $Q$  is  $5 \times 10^{-5}$   $C/cm^2$  (13). Although PMMA is capable of high resolution, its sensitivity  $Q$  is too low for commercial utilization in EBL.

Our approach to the development of a more sensitive positive resist is to retain the basic known degrading structural unit  $-(CH_2-C(X)Y)_n$ , but to replace the X or Y group (e.g.,  $CH_3$  for PMMA). By substituting electron-withdrawing or electronegative groups at X or Y, we hoped to weaken the energy required for degradation and to increase resist sensitivity. This effect is found experimentally for molecular organics. The C-C bond energy in  $CH_3-CO-CO-CH_3$ , for example, is 60 kcal/mole, compared to 83 kcal/mole for  $H_3C-CH_3$ ; the electronegative oxygen substituents on the carbons reduce the C-C bond energy by 28%.

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Following this polymer selection criterion, four basic vinyl polymers, poly(methacrylonitrile)(PMCN)  $\text{-(CH}_2\text{-C(CH}_3\text{) CN)}$ , poly(methyl alpha-chloroacrylate)(PMCA)  $\text{-(CH}_2\text{-C(Cl)CO}_2\text{CH}_3\text{)}$ , copolymer P(MCA-co-MMA), and copolymer P(MCN-co-MCA), have been studied at the basic level. PMCN represents a substitution of the Y substituent with an electron-withdrawing cyano (CN) group and PMCA represents a substitution of the methyl(CH<sub>3</sub>) group at X with electronegative chlorine (Cl). In addition, poly(isobutyl methacrylate)  $\text{-(CH}_2\text{-C(CH}_3\text{) CO}_2\text{CH(CH}_3\text{)}_2\text{)}$  was studied to determine the effect of the bulky ester alkyl group; poly(alpha-hydroxy isobutyric acid)  $\text{-(C(CH}_3\text{)}_2\text{-COO)}$  was selected and studied to determine if the polyester unit  $\text{-(COO)}$  combined with the well-known degrading quaternary carbon unit  $\text{-(C(CH}_3\text{)}_2\text{)}$ , could enhance G<sub>s</sub> or Q over those values of PMMA reference. Results of these basic radiation studies are found in Table I.

PMCA and P(MCA-co-MMA) are seen to be 2-4X more susceptible to radiation degradation than PMMA (14). Higher radiation degradation susceptibility is also observed for PMCN (15) and P(MCN-co-MCA). Direct e-beam testing is warranted for all these systems. In contrast, poly(alpha-hydroxy isobutyric acid) (16) and poly(isobutyl methacrylate) (17) were found to be less susceptible to radiation degradation than PMMA, and e-beam testing was not warranted.

Similar basic radiation studies of positive resists poly(butene-1-sulfone) (18), poly(isobutylene) (10), and poly(alpha-methyl styrene) (20) were the foundations for several of the results listed in Table I.

#### E-BEAM RESIST TESTING RESULTS

##### Positive Resists

Negative e-beam resists possess lower intrinsic resolution capability than positive resists; therefore, the ETDL resist program has dealt mainly with positive resist development -- except for one system (see Negative Resist Section). In addition, negative resists exhibit stronger tendencies to swell during development processing, which tends to lead to bridging of written features and resist distortions (21). Utilization of negative resists for direct-write e-beam lithography in the submicron domain will probably be excluded.

Following our basic radiation studies where higher G values were observed for PMCA versus PMMA reference (14), we determined that PMCA functioned as a more sensitive positive resist (22) than PMMA. Informal collaboration with Texas Instruments (TI) group working under ECOM contract #DAAB07-75-C-1297 led to further testing of PMCA; TI

TABLE I. G values and e-beam sensitivities for known positive resist polymers.

Positive Resist System	$G_S - G_X$	$G_S$	$G_X$	G (rads)	$Q, C/cm^2$	Lab
Poly(alpha-methyl styrene)	--	0.3	--	0.05	$1 \times 10^{-4}$	BTL <sup>a</sup>
Poly(alpha-hydroxy isobutyric acid)	0.30	0.37	0.07	--	not studied	ETDL <sup>b</sup>
Poly(isobutyl methacrylate)	1.1	1.1	0	--	low $G_S$ value	ETDL; HRC <sup>c</sup>
PMMA	1.3	1.3	0	1.9	$5 \times 10^{-5}$	IBM <sup>d</sup>
Poly(isobutylene)	--	4.0	--	2.5	$2 \times 10^{-5}$	BTL; ETDL
Poly(methyl alpha-chloroacrylate) (MCA)	5.4 <sup>e</sup> (2.3) <sup>f</sup>	6.0 <sup>e</sup> (3.2) <sup>f</sup>	0.7 <sup>e</sup> (0.5) <sup>f</sup>	5.7	$1 \times 10^{-5}$	ETDL; HRC <sup>g</sup> TI <sup>h</sup>
Poly(MCA-co-MMA)	2-3	3.1	0.06	3.1	$3-6 \times 10^{-6}$	ETDL; HRC
Poly(methacrylonitrile) (PMCN)	3.3	--	--	--	$7 \times 10^{-6}$	ETDL; HRC
Poly(MCN-co-MCA)	4-5	--	--	--	$4-7 \times 10^{-6}$	ETDL
Poly(MCN-co-MMA)	--	2-3	--	--	$1.2 \times 10^{-5}$	ETDL
Poly(butene-1-sulfone)	--	12	--	3	$3-5 \times 10^{-6}$	BTL
					$1-4 \times 10^{-6}$	BTL

<sup>a</sup> BTL - Bell Labs<sup>b</sup> ETDL - Electronics Technology & Devices Laboratory (ERADCOM)<sup>c</sup> HRC - Honeywell Research Center<sup>d</sup> IBM - International Business Machines<sup>e</sup> G value observed at low doses<sup>f</sup>, <sup>g</sup> G value observed at high doses<sup>h</sup> TI data from ETDL report #DAAB07-75-C-1297<sup>h</sup> TI - Texas Instruments<sup>i</sup>  $\bar{M}_n$  was only  $1.2 \times 10^5$  for this resist; an increase of three or four in  $\bar{M}_n$ , however, will increase Q to  $3-4 \times 10^{-6} C/cm^2$ .

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found the resist to be even more sensitive than reported by ETDL (see Table I). This resist is currently undergoing advanced device production testing under ERADCOM contract #MMT-76-C-8105. Although this polymer is less sensitive than the Bell Labs licensed poly(butene-1-sulfone) resist (see Table I), it possesses superior shelf-life stability, substrate adhesion, and ion-etch "dry-processing" compatibility. PMCA does, however, crosslink to some extent as determined by the  $G_x=0.5-0.7$  value from the basic studies, but this does not seriously impair its positive resist behavior. This deficiency can be overcome, at the expense of  $G_s$ , by utilization of the P(MCA-co-MMA) copolymer system. The basic study results of Table I show that  $G_s$  is decreased about twofold while  $G_x$  is decreased about tenfold. This explains why Lai et al (23) of Honeywell were able to observe better Q values for their P(MCA-co-MMA) copolymer systems than for their MCA homopolymer resist sample. Our earlier basic studies with P(MCA-co-MMA) helped lay the groundwork for their results and they referenced our study (24).

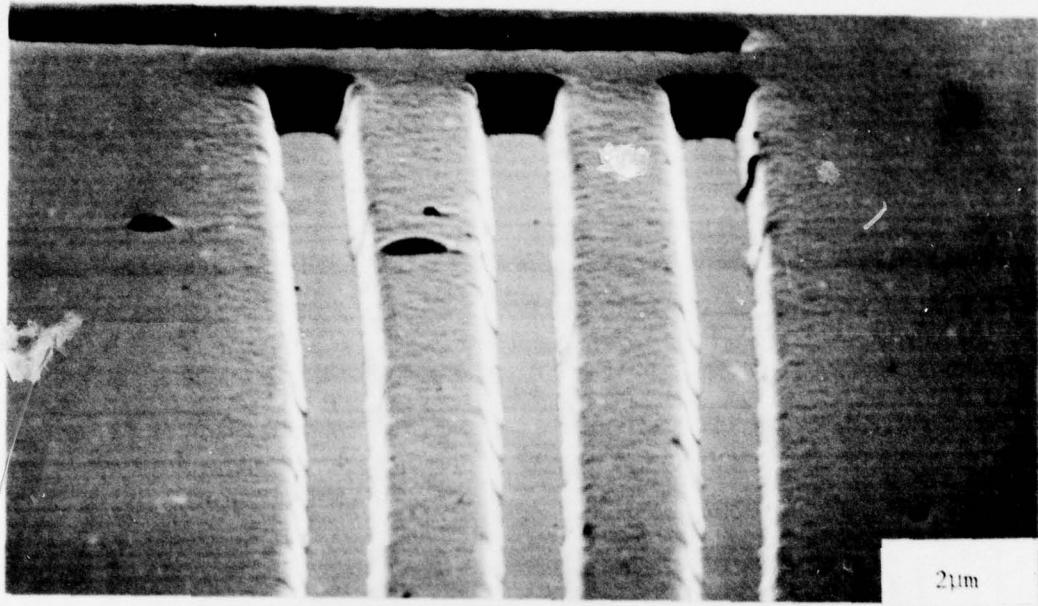
The G values of Table I for PMCN and P(MCN-co-MCA) dictated direct e-beam testing for these systems. They are found to function as sensitive positive resists. See Figure 3 for sample e-beam etched patterns for these systems. Preliminary measurements indicate, that Q is  $4-8 \times 10^{-6}$  C/cm<sup>2</sup> for PMCN and  $1-2 \times 10^{-5}$  C/cm<sup>2</sup> for the copolymer (70% MCA - 30% MCN). It should be emphasized here that Q is strongly a function of development processing, and that these processes require a considerable amount of research to produce optimization. Following our lead into the MCN polymer resist formulation (25), Bell Labs independently reported (26) that P(MCN-co-MMA) functions as a very sensitive positive e-beam resist (see Table I).

#### Negative Resists

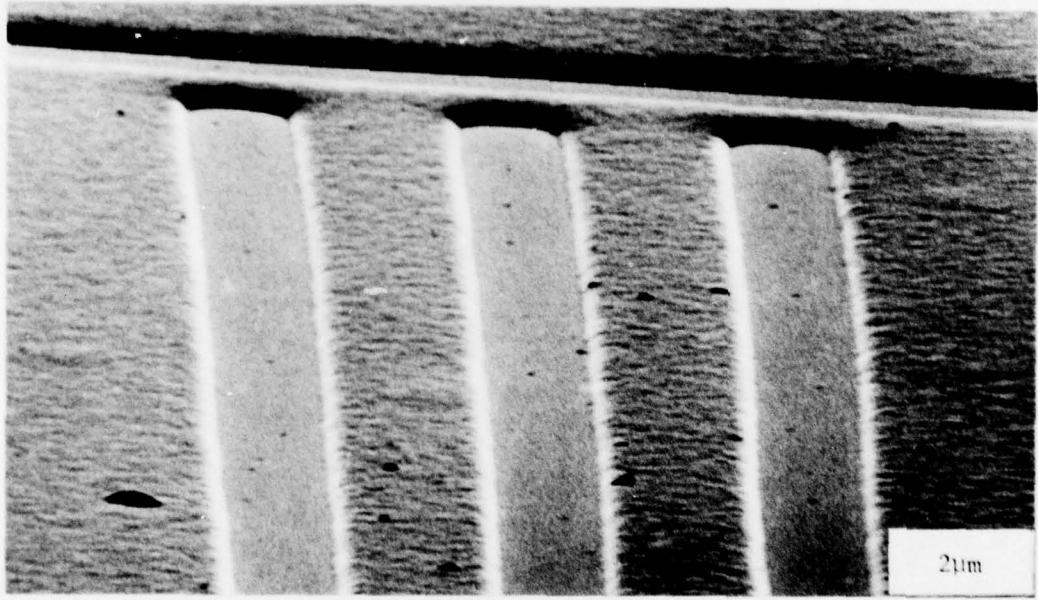
Positive resists act as high-resolution negative resists when overexposed. The doses required, however, are usually 1.5-2 orders of magnitude higher than usual. Poly(alpha-chloroacrylonitrile) (PACAN)  $\text{--CH}_2\text{--C}(\text{C}_1\text{CN})\text{--}$ , an early ETDL test positive system, changes resist behavior at significantly lower electron charge densities. The Q value at 10 keV is found in Table II. Although PACAN is not as sensitive as the Bell Labs P(GMA-co-EA) system, it is more sensitive than the TI polystyrene resist (27) and is capable of high resolution (see Figure 2).

PACAN must crosslink at the alpha-chlorine site (i.e., the X site). Chlorine removal (i.e., C-Cl bond cleavage) evidence for irradiated poly(vinyl chloride)  $\text{--CH}_2\text{--C}(\text{ClH})\text{--}$ , and Penton  $\text{--CH}_2\text{--C}(\text{CH}_2\text{Cl})_2\text{--CH}_2\text{--O--}$  is well established (28,29). Although the

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A



B

Figure 3. Scanning electron micrographs of developed electron-beam etched lines in (A) poly(methacrylonitrile) and (B) the copolymer poly(methacrylonitrile-co-methyl alpha-chloroacrylate).

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C-Cl bond is weaker than the C-C bond in these polymers, there is evidence that the chlorine in Penton is cleaved off by a dissociative electron capture reaction (29) which is thermodynamically favorable (30). Negative resist behavior for PACAN may also be the result of a low glass transition temperature,  $t_g$ . It is notable that structurally similar PMMA, PMCA and PMCN all have  $t_g$  values above 100 C and the crosslinking reactions for these polymers are strongly suppressed.

TABLE II. Negative e-beam resist sensitivities for four representative systems.

Resist System	$Q$ at 10 kV, $C/cm^2$	Lab
Polystyrene	$2 \times 10^{-4}$	TI <sup>a</sup>
PACAN	$5 \times 10^{-5}$	ETDL <sup>b</sup>
P(GMA-co-S)	$5 \times 10^{-6}$	HRC <sup>c</sup> ; BTL <sup>d</sup>
P(GMA-co-EA) (COP)	$4 \times 10^{-7}$	BTL <sup>d</sup>

<sup>a</sup> Texas Instruments

<sup>b</sup> Electronics Technology and Devices Lab (ERADCOM)

<sup>c</sup> Honeywell Corporate Research Center

<sup>d</sup> Bell Labs

#### RESIST SUMMARY

Only two e-beam resists, one negative (COP) and one positive (poly(butene-1-sulfone)), are commercially available. These two resists offer high sensitivity, but are beset with undesirable properties as well. The best positive resist, excluding sensitivity, is still standard PMMA. The ETDL positive test systems, PMCA and PMCN, are not optimized to the extent of the Bell Labs commercial resists, but preliminary results are very encouraging and advanced testing warranted. PMCA and P(MCA-co-MMA) resists have higher ion-etch compatibilities and possess potential as dry-process submicron production resists.

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Much in-depth research is still needed, both at the basic and production levels, to insure attainment of a suite of resists with desirable and diversified properties suitable for specific large scale integration devices.

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